Explicit Equation to Calculate the Liquid-Vapour Equilibrium for Ternary Azeotropic and Non Azetropic Systems

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In many cases, it is interesting to have the possibility of using explicit equation to calculate or reproduce the phase equilibrium compositions, particularly when dealing with optimization algorithms to simulate or design separation processes or their industrial equipment such as distillation and extraction columns, etc. [1-4].

In the present work, we present a new set of equations that can reproduce the VLE very accurately for azeotropic and non azeotropic ternary systems:

$$YY_1 = \frac{x_1}{a_1x_1 + b_1x_2 + c_1x_3} \qquad YY_2 = \frac{x_2}{a_2x_1 + b_2x_2 + c_2x_3} \qquad YY_3 = \frac{x_3}{a_3x_1 + b_3x_2 + c_3x_3}$$

$$y_1 = \frac{YY_1}{YY_1 + YY_2 + YY_3} \quad y_2 = \frac{YY_2}{YY_1 + YY_2 + YY_3} \quad y_3 = \frac{YY_3}{YY_1 + YY_2 + YY_3}$$

where x_i and y_i are the composition of the conjugated liquid and vapour phases in equilibrium, and the subscript *i* refers to the different component of the mixture.

We can observe that these equations have 9 correlation parameters (a_i, b_i, c_i), which have to be positive. They can be used to reproduce the equilibrium of the followings systems yielding a very good results comparing with classical thermodynamic models as NRTL:

- 2-butanol + 2-butanone + water at 600 mmHg (33 points)
- 2-butanone + 2-propanol + water at 760 mmHg (17 points)
- acetone + 2-butanone + water at 760 mmHg (37 points)
- 2-propanol + diisopropylamine + water at 760 mmHg (26 points)
- 2-propanol + water + toluene at 760 mmHg (34 points)
- water + 1-propanol + 1-butanol at 762 mmHg (16 points)
- ethanol + water + chlorobenzene at 760 mmHg (25 points)
- dietilether + ethanol + water at 2156,30 mmHg (39 points)
- dichloromethane + 2-butanone + water at 750 mmHg (25 points)

In this point it is important to remark that the proposed equations avoid the iterations in the equilibrium calculation steps inside the complex algorithm of design and simulation of separation processes, or even in the calculation of the distillation boundaries of azeotropic ternary systems.

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Summary

A new set of explicit equations to calculate the composition of a vapour in equilibrium with a given liquid mixture at a given pressure, and its bubble temperature has been developed. The proposed equations have been applied satisfactorily to different type of ternary liquid-vapour equilibriums and can be of great interest in complex calculations such as optimal design of multicomponent distillation columns, distillation column sequences and distillation boundaries in azeotropic systems [1,2].The explicit equations avoid the need of iterative calculations and the corresponding convergence problems associated to the non-linear equations involved.

1. Proposed equations

A new set of explicit equations capable of reproducing the VLE very accurately for both azeotropic and non azeotropic ternary systems are

$$y_i = \frac{x_i}{\sum_{j=1}^{3} a_{i,j} x_j} \Big/ \frac{x_q}{\sum_{j=1}^{3} a_{q,j} x_j} \qquad (1)$$

$$T = T_0 + \sum_{i=1}^{3} T_i \frac{x_i}{\sum_{j=1}^{3} a_{i,j} x_j} \qquad (2)$$

Where:
x_i and y_i are the composition of the conjugated L and V phases
i,j,q refer to the different components of the mixture
a_{ij} represent the 9 correlation parameters of eq.1, $a_{ij} > 0$.
T_0, T_1, T_2 and T_3 are the13 correlation parameters of eq. 2.

An optimization method (i.e. "Solver" of Excel) determinates the parameters of eqs. (1) and (2) providing the minimum of the objective function (O.F.) defined as in DECHEMA Collection Series [3]:

$$O.F. = \min \sum_{n}^{NP} \sum_{i} \left(\frac{\gamma_{i,exp} - \gamma_{i,cal}}{\gamma_{i,exp}} \right)^2_n \qquad (3)$$

The suggested procedure allows calculating the vapour composition y_i from the known composition of the liquid x_i and can be used in azeotropic and non-azeotropic systems (Fig.1and 2):.

Where: $\gamma_i = \frac{y_i \cdot P}{x_i \cdot P_i^{\circ}(T)}$

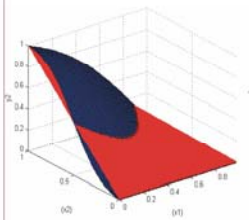

Figure 1. 3D y-x composition diagram for a hypothetic azeotropic ternary system (a_{ij}=0.1;a_{ii}=1). T he point's trajectory where the equilibrium surface intersects to the diagonal plane contains the possible azeotropic points.

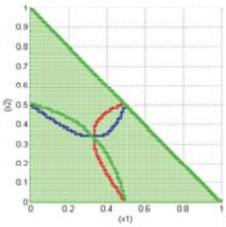

Figure 2. Projections of the 3D trajectories $y_i = x_i$ Their crossing points determine the binary and ternary azeotropes present.

In order to validate the goodness of the proposed equations, the following 12 systems from the Data Collection of DECHEMA Chemistry Data Series have been correlated and compared with the results obtained with the NRTL model:

- System 1: 2-butanol + 2-butanone + water at 600 mmHg
- System 2: 2-butanone + 2-propanol + water at 760 mmHg
- System 3: acetone + 2-butanone + water at 760 mmHg
- System 4: 2-propanol + diisopropylamine + water at 760 mmHg
- System 5: 2-propanol + water + toluene at 760 mmHg
- System 6: water + 1-propanol + 1-butanol at 762 mmHg
- System 7: ethanol + water + chlorobenzene at 760 mmHg
- System 8: dichloromethane + 2-butanone + water at 750 mmHg
- System 9: water + ethanol + toluene at 760 mmHg
- System 10: dietilether + ethanol + water at 2156,30 mmHg
- System 11: ethanol + water + 1-butanol at 760 mmHg·
  System 12: ethanol + acetone + chloroform at 760 mmHg

2. Results and discussion

Table 1 shows the parameters (a_{ij}, T_0 and T_i,) correspoding to empirical equations (1 and 2) used to calculate the LVE y_i and T. This table also shows the O.F. values obtained with the suggested equations in comparison with NRTL. NP is the number of experimental tie lines.

Results obtained show that the proposed equations yield good results comparing with NRTL.Figure 3 illustrates the capability of the proposed equations for systems 1 and 3.

System (NP)			a_{ij} i \ j 1	2	3	T_i	O.F (eq. 3) Explicit eq. 1 and 2	NRTL eq.
1		0				101.19892		
(33)	i	1	1.00000	0.32928	0.27333	-15.21353		
		2	0.78069	0.38523	0.04952	-10.53304		
		3	0.00769	0.00207	0.56650	-3.08851	0.5929	0.6771
2		0				91.02623		
(17)	i	1	1.00000	1.24077	0.42669	-18.44183		
		2	0.08928	0.28176	0.37813	0.75217		
		3	0.00861	0.04171	0.93205	2.03175	1.1047	1.6923
3		0				0.01219		
(37)	i	1	1.00000	2.07112	0.88989	57.58147		
		2	2.78604	4.08766	1.66643	268.74404		
		3	0.00000	0.00000	5.84273	35.02916	2.2526	1.8776
4		0				88.12457		
(26)	i	1	1.00000	0.63256	0.49809	-5.43670		
		2	0.72048	0.91069	0.14341	-6.18580		
		3	0.23959	0.00000	1.39421	-6.02133	0.5516	0.4770
5		0				100.10593		
(34)	i	1	1.00000	0.24045	0.50989	-8.77054		
		2	1.20470	2.51494	0.00238	-41.04073		
		3	0.91632	0.01310	2.85898	-19.76281	0.4250	0.3829
6		0				104.06898		
(16)	i	1	1.00000	0.27070	0.00000	-15.67350		
		2	0.02754	0.57531	1.42560	-0.50342		
		3	0.82225	2.72193	5.66194	-11.97997	0.5015	0.2933
7		0				107.64521		
(25)	i	1	1.00000	0.07241	0.59698	-16.93860		
		2	0.06449	1.22600	0.00000	-13.59610		
		3	0.00915	0.06090	4.87938	-31.01668	3.6231	4.1245
8		0				0.00376		
(25)	i	1	1.00000	20.58837	0.00000	120.17137		
		2	7.33219	21.14358	2.33452	1857.88919		
		3	0.00000	0.02874	32.52887	-296.71116	7.2495	5.3586
9		0				110.67754		
(16)	i	1	1.00000	0.16932	0.00000	-8.79464		
		2	0.11582	0.62443	0.18833	-11.28804		
		3	0.00000	0.31546	1.44450	-30.67265	0.8385	1.0300
10		0				1860.10399		
(39)	i	1	1.00000	5.46449	2.05761	-1796.86316		
		2	0.43832	2.55206	0.36220	-4559.36773		
		3	0.00217	0.00000	12.33606	412.18966	23.0589	35.3755
11		0				90.66512		
(32)	i	1	1.00000	0.38996	7.29154	-9.97970		
		2	0.49456	4.32645	0.00000	-25.04419		
		3	3.13700	0.89732	16.08352	70.99493	2.3500	3.0264
12		0				100.62008		
(51)	i	1	1.00000	2.05606	0.80440	-21.45777		
		2	1.18609	2.75311	0.60920	-23.99655		
		3	0.27119	0.00000	1.60708	-8.16243	0.2304	0.2246

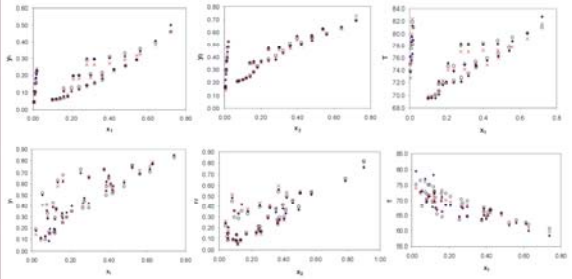

Figure 3. Illustration of the capability of the porposed equations.
System 1: a) y_1 vs x_1; b) y_2 vs x_2; c) T vs x_1. System 3; d) y_1 vs x_1; e) y_2 vs x_2; f) T vs x_1.

System 1 (a-c) is an example of a system which is more accurately regressed using the proposed equations. System 3 (d-f) shows a case where NRTL provides better results in the T data fitting while composition deviations obtained are similar with both models.

3. Conclusions

It can be concluded from the results obtained that the proposed equations yield very good results comparing with classical thermodynamic models as NRTL, showing similar deviations. What is more important, the proposed equations are explicit and thus avoid the iterations in the equilibrium calculations. Consequently, they may greatly simplify the algorithms of design and simulation of separation processes and the calculation of the distillation boundaries of azeotropic ternary systems.

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